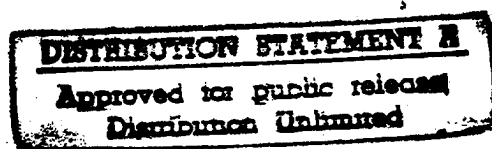# THE PHYSICAL CHEMISTRY OF CONCENTRATED OZONE. VI

THE EXPLOSIVE SENSITIVITY OF OZONE-OXYGEN

SOLUTIONS WITH RESPECT TO HEAT IMPULSES

- USSR -

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THE PHYSICAL CHEMISTRY OF CONCENTRATED OZONE. VI.
THE EXPLOSIVE SENSITIVITY OF OZONE-OXYGEN SOLUTIONS WITH RESPECT TO HEAT IMPULSES

Not a single investigation has been reported to date on the dependence of the explosive susceptibility of any liquid substances on the dilution by indifferent diluents, the molecules of which do not participate in the chemical process of explosive decomposition. An investigation of such a dependence, using ozone-oeygen solutions as an example, is the most convenient because the sensitivity of pure ozone has been determined sufficiently accurately [1]. In addition, the sensitivity of ozone is sufficiently high, so that experiments can be carried out in laboratory conditions, by confining oneself to weak actions on the explosive substance and by consuming small amounts of the latter.

In the present investigation the explosion susceptibility of liquid ozone-oxygen mixtures in response to heat pulses was investigated by the method of burning wires, over a broad range of concentrations of an indifferent diluent, namely oxygen.

Experimental Part

Experimental Procedure. Experiments with Small Amounts of Matter

The investigated ozone-oxygen solutions of required concentration were sealed in glass ampoules, so that it was possible to mix thoroughly before the experiment each batch of solution, keeping it perfectly pure.

A thin (20-30 microns) tungsten wire, wound in a

spiral on a thicker (0.3 mm) molybdenum wire, was sealed beforehand into a ready-made ampoule made of molybdenum glass. During the sealing process, a stream of nitrogen was passed through the ampoule to prevent oxidation of the strongly heated metal. Then a mixture of acids (nitric -- 5 parts by volume, sulfuric -- 3 parts, water -- 2 parts) was placed in the ampoule to dissolve the molybdenum wire without affecting the tungsten. An ampoule with a thin tungsten wire inside was thus obtained. The residues of the thick molybdenum wire, still retained in the sealing points and protruding outward from the ampoule, provided reliable electric contact during the burning of the tungsten wire and guaranteed that it would be burned of necessity inside the ampoule.

The ampoule was sealed to the setup used to obtain pure ozone gas. After verifying (with the aid of a vacuum) the quality of the seal between the wire and the ampoule, the pure gaseous ozone and oxygen were condensed in sequence in the necessary amounts. The amounts of these components were measured by measuring the pressure in a measuring container of one liter capacity, filled alternately with ozone gas or oxygen gas. Then the ampoule with the liquid mixture of these substances was sealed away from the setup and transported in a Dewar flask with liquid nitrogen to the place where the explosion susceptibility was measured.

The stirring and the exploding of the ampoules were realized behind a reliable shield. The ampoule was placed in a manipulator, which made it possible to stir the contents by rotating it in a large Dewar flask filled with liquid nitrogen or with liquid oxygen. After a prolonged stirring, the ampoule was taken out rapidly, with the aid of the same manipulator, from the Dewar flask and carried to metallic plates which served as electric contacts. The outer molybdenum leads from the ampoule were brought in contact with the plates, causing an electric circuit to be closed, and a short electric pulse was passed through the tungsten wire inside the ampoule; the pulse burned the wire. At the same time, the presence or absense of an explosion were registered. The transporting of the ampoule from the Dewar flask to the electric contacts was completed within not more than one second; therefore, there was no evaporation or noticeable heating of the contents.

To burn the wire, alternating or direct current at voltages up to 200 v was used. An additional relatively large resistance (20 ohms) was connected in series with the circuit, and this determined essentially the current in the circuit, and made it little dependent on variations of the resistance of the burned wires during the process of their heating by the current.

In the absence of explosion, one could observe inside the ampoule a bright flash of the burning wire and a splash of liquid.

Nevertheless, the flow of current through the wire was monitored in addition with an oscillograph. If there was no explosion, the current was turned on again in order to verify once more whether the wire inside the ampoule actually burned out.

Experiments With Large Amounts of Substance.

To test ozone-oxygen solutions of relatively low concentrations, stronger heat pulses were necessary and considerably greater amounts of the investigated substance in each test (up to 150 cm^3); and, therefore, experiments with them were carried out in an especially equipped room, and the vessels with ozone were located behind reliable shielding during the entire time of operation.

The ozone-oxygen mixture for these experiments was condensed in a coil cooled with liquid oxygen; the condensate ran off from an open vessel, which was also cooled. To avoid freezing of the air, which could have introduced moisture in other contaminations into the condensate, the vessel was subjected to a flow dry oxygen during the entire experiment. The resultant ozone-oxygen solution, containing several percent of ozone, was then concentrated by gradually reducing the cooling (the cooling Dewar flask was gradually lowered).

To accelerate the evaporation and to produce stirring, oxygen gas was bubbled through the solution. At the instant of testing explosion susceptibility, the solution was at its boiling temperature, at which no stratification of the liquid took place [2].

The concentration was measured by the ε-method [3]. The capacitive transducer was removed at the required instant from the vessel with the solution, to protect it from the action of the explosion.

The heat pulse during these experiments was transmitted to the ozone by burning in it a constantan wire 50 microns in diameter, or a nichrome wire 300 microns in diameter.

Calculation of the Energy of the Heat Impulse.

For each series of experiments, the values of the energy of the primary heat pulses were calculated. These

consisted of two components:

1) energy of combustion (oxidation) of the material of the wire;

2) Joule heat liberated in the wire by the passage of the current.

The energy of combustion E_1 can be calculated with sufficient accuracy, since the quantities necessary for this purpose, namely the amount of metal and the heat effect of oxi ation, are known. Since a considerable amount of energy is liberated during the oxidation of metals, the difference in the thermal effect of oxidation by oxygen or ozone is relatively small, and can be neglected.

The Joule heat E_2 can be calculated by two methods.

1) By means of the formula

$$E_2 = 0.24 \ i^2 r t \ cal$$

where E^2 [sic] is the current strength, equal to V/R; R is the resistance of the entire circuit, which remains approximately constant; t is the time of current flow, measured with the aid of the oscillograph; r is the resistance of the burned wire. Since r changes during the time of heating, it becomes necessary to take its average value in the interval from the initial temperature up to the melting temperature of the metal. Such a calculation is naturally approximate, but it can be verified by a second method.

2) It can be assumed that the Joule energy is approximately equal to the energy necessary to heat the wire to melting, considering that the melting stops the flow of the current. Then E_2 can be calculated knowing the specific heat and the melting heat of the metal.

The values of E_2, calculated on the basis of 1(and 2), were somewhat different: for example, for a 27 micron tungsten wire (experiments of series 5) $E_2(1) = 0.047$ cal, $E_2(2) = 0.017$ cal, and the average value used was $E_2 = 0.032$ cal.

However, such a discrepancy is insignificant, since E_2 remains a small fraction of the total energy E (in this example, E = 0.15).

Table 1

Серия 1		Серия 2		Серия 3	Серия 4								Серия 5			Серия 6		Серия 7	
Концентра-ция	Результат	Концентра-ция	Результат	Концентра-ция	Напряжение	Концентра-ция	Результат	Напряжен.	Концентра-ция	Результат	Напряжен.	Концентра-ция	Результат	Напряжен.	Концентра-ция	Результат	Концентра-ция	Результат	Концентра-ция	Результат

Серия 1: Концентрация: 63,5 / 60 / 52,5 / 50 / 24 / 15 — Результат: + + + + + +

Серия 2: Концентрация: 20 / 21 / 29 / 38,5 / 46 / 50 / 52,5 / 53,5 — Результат: − − − − − − + +

Серия 3: Концентрация: 55,5 / 72,5 / 73 / 74,5 / 76 / ~1 / 90 — Результат: − − − − − + +

Серия 4:
- Напряжение: 14,5 / 28 / 40 / 57 / 63 / 74 / 90 / 90 / 90; Концентрация: 75 / 75 / 76,5 / 72,5 / 73,5 / 75,5 / 74,5 / 74,5 / 75; Результат: − − − − − − − − −
- Напряжение: 80 / 82 / 82 / 82,5 / 82,5 / 84 / 84 / 85 / 85; Концентрация: 75 / 73,5 / 73 / 71 / 75 / 75 / 75 / 75; Результат: − − + + + − − − +
- Напряжение: 85 / 87,5 / 90; Концентрация: 75 / 76 / 74,5; Результат: + + +

Серия 5: Напряжение: 90 / 90 / 120 / 150 / 165 / 175 / 180 / 185 / 200; Концентрация: 59,5 / 58,5 / 60 / 60 / 59 / 60 / 58 / 56 / 59; Результат: − − − − − − + + +

Серия 6: Концентрация: 18,5 / 27,5 / 35 / 50 / 60 / 65 / 75 / 90 — Результат: − − − − − − − +

Серия 7: Концентрация: 9 / 12,5 / 17,5 / 25,0 / 28 / 28 / 33 — Результат: − − − − − + +

1) series
2) concentration
3) result
4) voltage

*The + denotes an explosion; the −, the absence of an explosion.

Results of the Experiments

A total of seven series of experiments were performed, of which the first five were under laboratory conditions and the last two on larger scales.

Series 1.

The energy of the heat pulse remained constant, $E = 0.230$ cal/cm (tungsten, $d = 32$ microns, $l = 0.7$ centimeters, $V = 65$ volts with an additional resistance $R_{add} = 21$ ohms). The concentration (c) of the ozone of the mixture varied from 15 to 63 percent (Table 1)* The stirring was at -196°.

Explosions took place in all the experiments; the sound of the explosion weakened noticeably as the temperature was decreased.

The explosions in this series of experiments were obviously explained by the fact that at -196°C the mixture breaks up into two layers -- a heavy one, with an ozone concentration of approximately 76 percent, and a light one with a concentration of O_3 of approximately 7 percent (the figures are those given by Schumacher [2].)

Thus, in all the experiments, an explosive heavy layer was present in the lower portion of the ampoule. The amount of this heavy material decreased in the total concentration of the mixture.

From this series of experiments one can conclude that in the case of a heat pulse with the given energy, the concentration boundary of explosiveness lies below 76 percent of ozone.

Series 2.

The energy of the heat pulse E was the same as in Series 1. The concentration of the ozone varied from 20 to 53.5 percent. The stirring of the mixtures in the ampoules was carried out at the temperature of liquid oxygen (-183°C), which made it possible to obtain homogeneous solutions over a wider range of concentrations (region of stratification in this temperature, according to Schumacher, lies between 25 and 58 percent of ozone).

The explosiveness boundary under these conditions lies at a concentration below 52.5 percent of ozone. This value is lower than the upper boundary of stratification after Schumacher (58 percent). Since the boundary of explosiveness

*The percentages are always by weight.

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cannot be determined, if it is within the stratification interval, then either our value is not completely accurate, or else the upper boundary of stratification has been determined inaccurately by Schumacher.

Series 3.

$E = 0.70$ cal/cm (tungsten $d = 20$ microns, $l = 0.7$ centimeters, $V = 11.5$ volts and $R_{add} = 21$ ohms). The concentration was varied from 55.5 to 90 percent. Stirring at $-183°C$. The boundary of explosiveness lies below 81 percent of ozone.

Series 4.

Concentration constant -- approximately 75 percent ozone. The energy of the pulse varied (tungsten $d = 25$ microns, $l = 0.7$ centimeters, voltage from 14 to 90 volts at $R_{add} = 21$ ohms). Stirring at $-183°C$.

The explosiveness boundary of the 75 percent mixture corresponds under the given condition to 82 volts or 0.080 cal/cm.

Series 5.

Concentration constant, approximately 75 percent ozone. The pulse energy was varied (tungsten, $d = 27$ microns, $l = 0.7$ centimeters, voltage from 90 to 200 volts, $R_{add} = 21$ ohms). Stirring at $-183°C$.
The boundary of explosiveness for the 59 percent mixture under these conditions corresponds to 175 -- 180 volts or 0.150 cal/cm.

Series 6.

$E = 0.140$ cal/cm (constantan, $d = 50$ microns, $l = 1.0$ centimeters, $V = 10$ volts at $R_{add} = 0.5$ ohms). The concentration varied from 18.5 to 80 percent ozone. Stirring at $-183°C$.
The explosiveness boundary lies below 80 percent ozone.
Under the same conditions a stronger pulse was used in one experiment ($V = 100$ volts, $E = 2.5$ cal/cm). An explosion took place at a concentration of 45 percent ozone.

Series 7.

E = 9.7 cal/cm (nichrome, d = 300 microns, l = 10 centimeters, V = 150 volts at R_{add} = 1.4 ohms). The concentration varied from 9 to 30 percent ozone. Stirring at -183°C.

The explosiveness boundary is measured by concentration, lies below 28 percent ozone.

Discussion of the Results

Data on the explosion susceptibility of ozone-oxygen solutions with respect to different heat pulses are presented in Table 2.

The first three columns give the numbers of the series of experiments, the values of the concentration c of the solutions in % by weight, and the lowest values of the energy of the heat pulses, E in cal/cm, at which the explosion registered. The value of E includes the heat of oxidation (combustion) of the wire. The last columns give the time of current flow (t) in seconds and the power of the pulse (W = E/t in watts). The values of E and W are referred to 1 centimeter of wire length. The table includes data for 90 -- 95 percent of ozone (first row) obtained earlier [1].

Table 2

| Series No.	c, % by weight	E, cal/cm	t, sec	W, w/cm
—	90—95	0,001	0,001	4,2
3	81	0,07	0,001	290
6	80	0,14	0,02	29
4	75	0,08	0,001	340
5	59	0,15	0,0005	1260
2	52,5	0,23	0,01	96
6	45	2,5	0,01	1050
7	28	9,7	0,02	2000

The results of the experiments show that the explosion susceptibility of the ozone with respect to a heat pulse is greatly reduced upon dilution with oxygen. Whereas an energy of 10^{-3} cal/cm is sufficient for explosion of concentrated ozone, corresponding to heating of the wire to 210° [1], for an explosion of 75 percent of ozone this quantity increases by a factor of several times 10. In 75 percent ozone it is possible to burn a tungsten wire 20 microns thick without producing an explosion (series 4). 28 percent ozone can be exploded only with great difficulty.

The concentrations and the minimum energies necessary for the explosion are represented in the diagram in coordi-

nates log E — c. In spite of
the considerable spread in the
data, which is quite natural in
investigations of this kind, o-
ne can note that the points cha-
racterizing the boundary of ex-
plosiveness fit within a cer-
tain band, the lower edge of
which fits the equation log E
= 2.7 - 0.063 c, or E = 186
exp (-c/69), where E is in cal/
cm and c is in percent by
weight.

    The heat pulses with low-
er energies than called for by
the equation do not cause ex-
plosion of the given ozone-oxygen
mixture.

    It is obvious that this dependence loses its meaning
in the case of weak solutions, in which the explosion is in
general incapable of propagating.
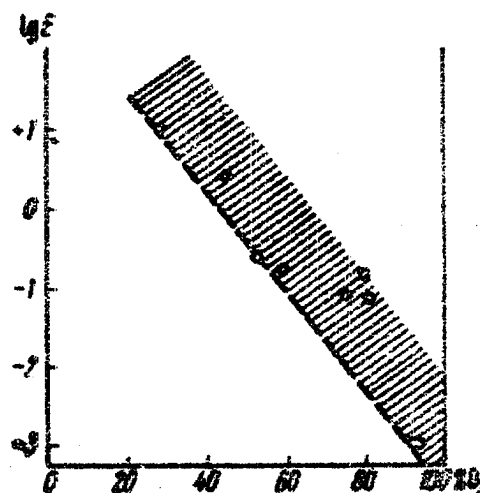
Conclusions

    The explosion susceptibility in response to heat pul-
ses of liquid ozone-oxygen mixtures containing ozone from 15
to 90 percent was investigated. A sharp reduction in the ex-
plosion susceptibility was observed on dilution with oxygen.
    A mixture with ozone concentration c (% by weight) will
not explode if the heat pulse has an energy E (cal) less than
called for by the equation $E = 186 \exp(c/6.9)$.

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